

Study on Effect of Coupling Agents on Underfill Material in Flip Chip Packaging

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Abstract—Coupling agents are widely used in order to improve the adhesion property of underfill. In this study, three different silane coupling agents, two titanate coupling agents, and one zirconate coupling agent were added into an epoxy underfill material. Their effects on the flow behavior and curing profile of the epoxy underfill were studied with a rheometer and a differential scanning calorimeter (DSC), respectively. The thermal stability of the cured underfill material was studied with a thermogravimetric analyzer (TGA). A thermal mechanical analyzer (TMA) and a dynamic mechanical analyzer (DMA) were used to measure the coefficient of thermal expansion (CTE), the glass transition temperature (T_g), and the storage modulus (E'). In addition, the adhesion of the underfill on benzocyclobutene (BCB) passivated silicon die and polyimide passivated silicon die was measured through die shear test. The effects of aging in an 85 °C /85% relative humidity chamber were also studied through moisture absorption test and die shear test.

Index Terms—Adhesion, BCB passivation, coupling agents, epoxy, polyimide passivation, silane, titanate, underfill, zirconate.

I. INTRODUCTION

FLIP chip technology is a new packaging approach, in which the integrated circuit (IC) chip is connected to substrate through solder joints with the active side facing down. It has an advantage of higher input/output (I/O) count as well as greater pitch due to its area array of interconnection. Also, fast signal propagation can be achieved due to its short interconnection path [1]. However, due to the great difference in coefficient of thermal expansion (CTE) between the silicon die and the organic substrate, thermal stress is generated on the solder joints during thermal cycling of the flip chip assembly. This stress on the solder joints can lead to failure of the interconnection. To prevent the failure of the solder joints, an underfill encapsulant adhesive (silica filled epoxy) is used to fill the gap between the IC and the substrate (board) to reduce stress on the solder joints [2]. By matching the CTE of the solder joints, the underfill material can provide a rigid and strong reinforcement without contributing additional stress to the joints. The introduction of an underfill adhesive between the die and the substrate can improve the solder joint fatigue life by orders of magnitude [2].

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The underfill provides environmental protection in addition to thermo-mechanical protection. There are several requirements for an underfill material, which include relatively high modulus, high glass transition temperature (approaching the highest temperature that the assembly is subjected to during use), low ionic concentration, low dielectric constant, low alpha particle emission, CTE matched to that of solder joint, low moisture absorption, and good adhesion at the various interfaces (interfaces with the chip passivation layer, solder mask on the board, and the solder joint). However, delamination (total loss of adhesion) between the die and the underfill in underfilled flip-chip assemblies is still a major concern for yield loss and reliability [3], [4]. The problem of delamination is particularly prevalent when the assembly is subjected to a thermal cycling in a high humidity environment. Delamination at the underfill/die or underfill/substrate interface can lead to cracking and corrosion of the interconnection [5]. There are many reasons for delamination such as: low adhesion due to incompatible surfaces, contamination, and void formation during curing.

The adhesion between the underfill material and the passivation layer is critical to the reliability of flip chip assemblies. In order to improve adhesion of underfill material with passivation on silicon die and organic substrates, coupling agents (CA) have been used. Die shear and aging test in an 85 °C/85% relative humidity chamber have been employed to study the adhesion strength [6]. Interfacial fracture toughness of the interfaces between various substrates and epoxy-based underfill material with different coupling agents was also investigated [7], and it was found that small amount of organofunctional silane coupling agents can alter the fracture toughness of the underfill/substrate interfaces. The coupling agents can affect the adhesion property of the underfill material, and they may also affect properties of the underfill material other than adhesion. The effect of coupling agents on flow behavior and contact angle of the underfill material on different substrates has been reported. Vinyl functionalized and epoxy functionalized silane coupling agents were found to be able to reduce the viscosity underfill and contact angles of the underfill resin on FR-4 printed circuit board [8]. However, the effects of coupling agents on properties of underfill material such as curing kinetics, thermal stability, thermal-mechanical property, and moisture absorption have seldom been reported. Yet, an understanding of the effects of coupling agents on those properties is necessary in order for coupling agents to be used in underfill material. Except silanes, titanate and zirconate coupling agents have not been explored to be used in underfill material. In this paper, the effects of three typical silane coupling agents, two titanate coupling agents, and

one zirconate coupling agent on adhesion property and various other properties of underfill are discussed.

II. EXPERIMENTAL

A. Materials and Underfill Preparation

Coupling agent (equal to 1.5% weight of the underfill) was added into an epoxy underfill system consisting of a cycloaliphatic epoxy resin, an acid anhydride as hardener, and cobalt(II) acetylacetonate as catalyst. The mixture was then stirred until it was homogeneous. The underfills were then stored in a freezer at -40°C when not used. Six different coupling agents CA-1 (epoxy silane, A187), CA-2 (amino silane, A1102), CA-3 (vinyl silane, A171), CA-4 (titanate, Lica38), CA-5 (titanate, Lica97), and CA-6 (zirconate, NZ97) were employed in this study. Fig. 1 shows their structures.

B. Characterization of Uncured Underfill

Viscosity Measurement: The viscosity of underfill material versus shear rate (1 to 100 s^{-1}) was recorded using a controlled stress rheometer (Model AR1000N, TA Instruments) at 25°C immediately after the underfill was prepared. The viscosity of underfills was measured again after the underfills were stored at -40°C for 45 days.

Curing Profile Analysis with Differential Scanning Calorimeter (DSC): About 10 mg of underfill material was sealed in a hermetic DSC pan. The curing profile was recorded with a differential scanning calorimeter (Model 2920, TA Instruments) with a heating rate of $5^{\circ}\text{C}/\text{min}$ under N_2 purge gas to determine any effect of coupling agent on the curing of underfill.

C. Die Shear Sample Preparation and Die Shear Test

Benzocyclobutene (BCB) passivated dies ($2.5 \times 2.5\text{ cm}$ and $2 \times 2\text{ mm}$) were cleaned according to the standard procedure mentioned in reference [9]. S200 polyimide (PI) passivated silicon dies of two sizes were used: $1.2 \times 1.2\text{ mm}$ and $1 \times 1\text{ cm}$. Glass beads (0.5% weight of underfill) with diameters of 75 microns were used as spacers to control the gap between the small die and the large die. A detailed die shear sample preparation procedure is given in reference [6]. For curing, the die shear samples were put into an oven, heated at a rate of $5^{\circ}\text{C}/\text{min}$ to 250°C , and the temperature of the oven was kept at 250°C for 30 min. Die shear test was performed 12 h after the curing of the sample. For aging test, the cured die shear samples were put in an $85^{\circ}\text{C}/85\%$ relative humidity (RH) chamber (85/85 aging) for 500 h, then the die shear test was performed. Die shear test was performed on a die bond tester (Model 550–100K, Royce Instruments) with a blade speed of 4 mil/s. The die shear strength is reported in MPa.

D. Thermomechanical Analysis and Moisture Absorption Test of Cured Sample

Thermo-Mechanical Test: A thermomechanical analyzer (TMA, TA Instruments, Model 2940) was used to measure the thermal expansion of cured underfill material under N_2 purge gas with a heating rate of $5^{\circ}\text{C}/\text{min}$. The dynamic mechanical analysis (DMA) of the cured underfill strips was performed in

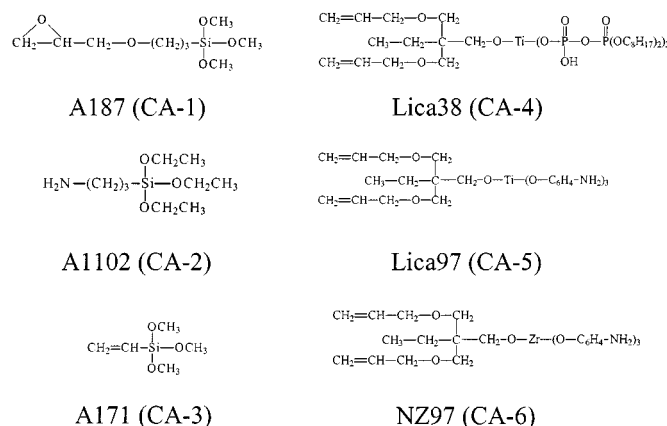


Fig. 1. Structures of coupling agents.

single cantilever mode under 1 Hz sinusoidal strain loading. The storage modulus E' , loss modulus E'' , and loss factor were recorded from room temperature to 250°C at a heating rate of $5^{\circ}\text{C}/\text{min}$. The thermogravimetric analysis (TGA) of the cured underfill was performed on a thermogravimetric analyzer (TA Instruments, Model 2940) under N_2 purge gas with a heating rate of $5^{\circ}\text{C}/\text{min}$.

Moisture Absorption: The underfill was cured in an aluminum pan with a diameter of 40 cm and diced into strips. Then the underfill strips were dried in a vacuum oven. The dried samples were weighed and then placed in an $85^{\circ}\text{C}/85\%$ RH chamber. The samples were taken out of the chamber at different intervals and weighed. Weight gain of underfill during aging in an $85^{\circ}\text{C}/85\%$ relative humidity chamber was defined as moisture absorption.

III. RESULTS AND DISCUSSION

A. Effect of Coupling Agents on Uncured Material

Viscosity Study: The viscosity of the underfill materials without CA was measured immediately after their preparation at 25°C . The underfill behaved as a Newtonian fluid with a constant viscosity of $0.16\text{ Pa}\cdot\text{s}$ in the tested shear rate range of 1 to 100 s^{-1} . With the addition of coupling agents, the characteristic Newtonian behavior was not changed. The viscosity varied from 0.14 to $0.22\text{ Pa}\cdot\text{s}$ for the underfills added with different coupling agents. As titanate and zirconate coupling agents are viscous fluids with high viscosity, addition of those coupling agents increased the viscosity of the system (Table I). Among them, the underfill material with coupling agent CA-6 showed the highest viscosity of $0.22\text{ Pa}\cdot\text{s}$.

The viscosity of the underfill materials was measured again after 45 days of storage at -40°C . The viscosity of the underfill without coupling agent, with CA-1, CA-2, or CA-3 did not show significant increase. However, the viscosity of the underfill with the addition of CA-4, CA-5, or CA-6 increased at an appreciable amount (Table I). Among them, the underfill material with coupling agent CA-6 showed the largest increase in viscosity (from $0.22\text{ Pa}\cdot\text{s}$ to $0.37\text{ Pa}\cdot\text{s}$). This indicated that coupling agent CA-6 probably could catalyze the curing reaction of the underfill even at a very low temperature, thus affecting the storage life-time of the underfill material.

TABLE I
VISCOSITY OF UNDERFILL MATERIAL

	Viscosity before storage (Pa-s)	Viscosity after storage (Pa-s)
With no CA	0.16	0.16
With CA-1	0.15	0.16
With CA-2	0.18	0.19
With CA-3	0.14	0.14
With CA-4	0.18	0.22
With CA-5	0.20	0.26
With CA-6	0.22	0.37

Effect on Curing of Underfill: As mentioned in previous paragraph, the underfill material with CA-6 showed the most significant increase in viscosity during storage at low temperature. It was suspected that the coupling agents might affect the curing of the underfill material. Therefore, DSC was used to study the curing of the underfill materials. Fig. 2 shows the curing profiles of the underfill materials recorded by DSC. Without any coupling agent, the curing started around 145 °C, and the peak temperature for curing was 194 °C. With the addition of the coupling agent, the curing profile changed. Addition of CA-6 led to curing at a lower temperature. The curing reaction of underfill with CA-6 started at temperature as low as 70 °C. Addition of CA-5 also led to a lower curing onset temperature. It can be concluded that CA-5 and CA-6 can catalyze the curing reaction. Both of those two coupling agents have amino groups, which can catalyze the curing reaction of epoxy. The addition of amino silane CA-2 also led to a slightly decrease in curing onset temperature. Most importantly, the zirconium in CA-6 affected the curing reaction to the greatest extent. Addition of CA-1 (epoxy silane) and CA-3 (vinyl silane) had no obvious effect on the onset curing temperature. Addition of coupling agent CA-4 had a retarding effect on the curing of the underfill material. With the addition of CA-4, the curing started around 160 °C, 15 °C higher than for the system without any coupling agent additive.

B. Bulk Property of Cured Underfill Material

Moisture Absorption: Fig. 3 shows the moisture absorption of the cured underfill material versus aging time in an 85 °C/85% relative humidity chamber. The base underfill formulation can absorb moisture significantly. The weight gain after 700 h is about 2.5%. The addition of silane did not significantly increase the moisture absorption. As a matter of a fact, the addition of CA-2, an epoxy silane, showed a lower moisture absorption. However, the addition of titanate and zirconate coupling agents increased the moisture absorption significantly. The weight gain after 700 h of aging was above 3.0% for the formulation with titanate and zirconate coupling agents. Among them, CA-6 increased the moisture absorption most significantly, and the weight gain after 700 h was as high as 3.6%. The higher moisture absorption of underfills with addition of titanate and zirconate coupling agent contributed to the decrease in their adhesion strength after aging 85 °C/85% RH, which will be discussed later.

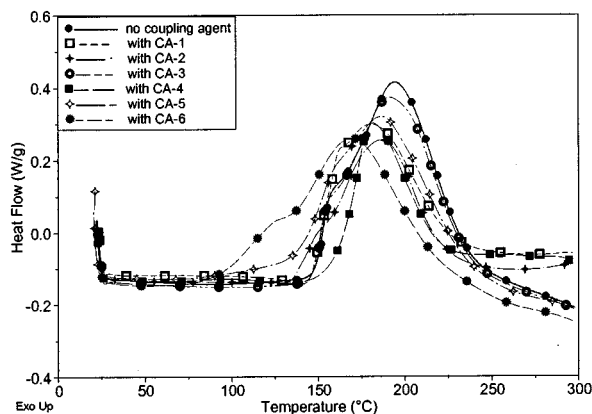


Fig. 2. DSC profile of curing of underfill material (heating rate: 5 °C/min, under N₂).

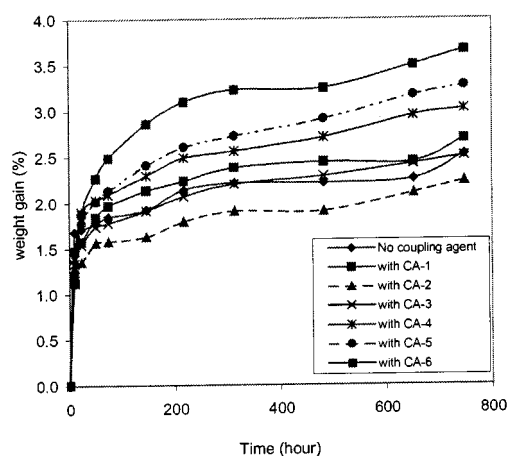


Fig. 3. Moisture absorption of cured underfill during aging in an 85 °C/85% relative humidity chamber.

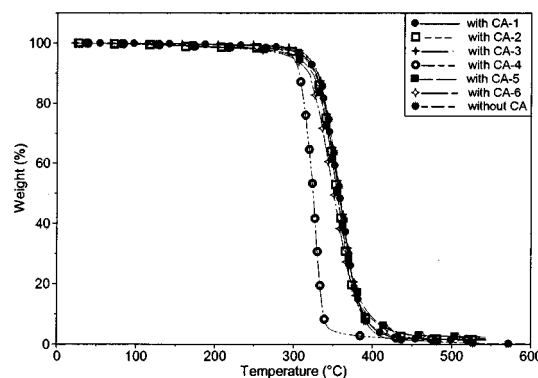


Fig. 4. TGA profile of underfill material (heating rate: 5 °C/min, under N₂).

Thermal Degradation Analysis: The TGA results of the underfills are shown in Fig. 4. The addition of different coupling agents did not significantly affect the onset temperature of weight loss. Interestingly, the addition of CA-4 substantially accelerated the weight loss of cured underfill. This is due to the pyrophosphate moiety in the structure of CA-4.

Thermomechanical Analysis: TMA tests were performed on the cured samples at a heating rate of 5 °C/min under N₂. The results are shown in Fig. 5. CTE of the cured underfill material did not change much after the addition of the coupling agents. The

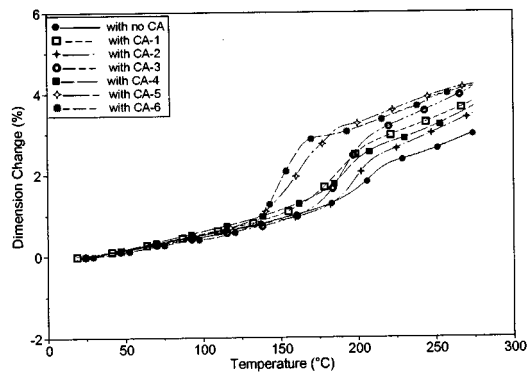


Fig. 5. TMA profile of underfill material (heating rate 5 °C/min under N_2).

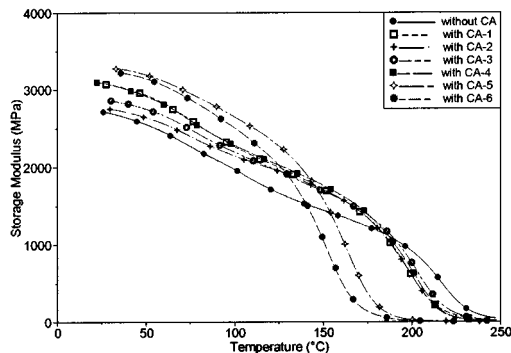


Fig. 6. DMA profiles of underfill materials (heating rate 5 °C/min).

onset temperatures of glass transition differed greatly. Without any coupling agent, the underfill material had the highest T_g of 190 °C. With addition of the coupling agents, the T_g decreased. Particularly, with the addition of CA-5 and CA-6, the T_g was 50 °C lower than that of underfill without any coupling agent. The addition of silane coupling agents also led to a decrease in T_g of the cured underfill, but the magnitude of the reduction was less. There are two reasons for the decrease in T_g . The unreacted coupling agents act as plasticizers in the polymer matrix, thus leading to a decrease in T_g . Particularly, the titanate and zirconate coupling agents have long aliphatic chains in their structures, and these long chains act as plasticizers even if they are chemically bonded to the polymer network.

Dynamic Mechanical Analysis: DMA tests were performed on cured underfill materials with a heating rate of 5 °C/min. The results are shown in Fig. 6. For the underfill materials, the onset temperatures of glass transition obtained from DMA were in the same order as those obtained with the TMA test. Without the coupling agent, the material showed the highest T_g . However, with the addition of CA-5 and CA-6, the T_g were much lower than that of underfill without coupling agent. With addition of CA-4 and silane coupling agents, the underfill showed T_g between that of underfill without any coupling agent and those of underfills with CA-5 or CA-6 added. The cured underfills with CA-6 and CA-5 showed higher moduli than the underfill without any coupling agent.

C. Adhesion with Different Passivation Layer on Silicon Die

In order to investigate the effect of the coupling agent on the adhesion properties, the die shear samples were prepared with

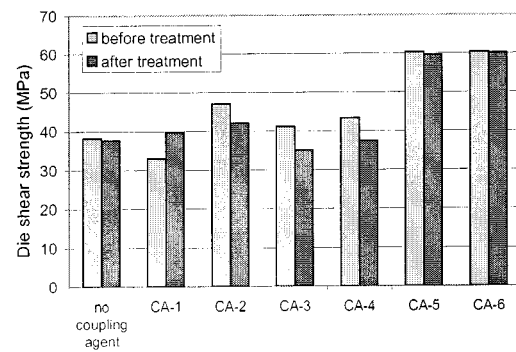


Fig. 7. Die shear strength of underfill with BCB passivated die with and without UV/O₃ treatment.

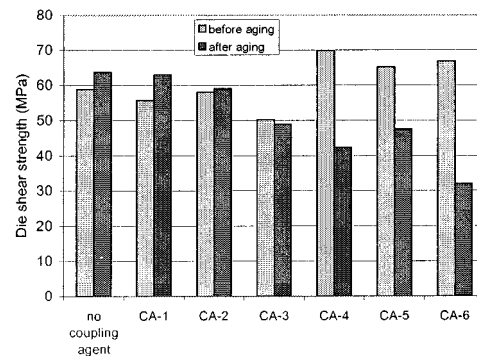


Fig. 8. Die shear strength of underfill with polyimide passivated silicon die before and after aging at 85 °C/85% relative humidity chamber for 500 h (die size 1.2 × 1.2 mm).

the underfill materials. Two sets of BCB passivated silicon were used. The first set of BCB passivated dies were cleaned without further UV/ozone treatment. And the second set of BCB passivated dies were treated with UV/ozone after cleaning. The die shear test results are shown in Fig. 7. The addition of coupling agent CA-1 did not improve the adhesion of underfill to BCB passivation. While addition of coupling agents CA-5 and CA-6 led to significant increases in the adhesion of underfill to BCB passivation.

Another set of die shear test samples were prepared with BCB passivated silicon die treated with UV/ozone after cleaning. The test results are also shown in Fig. 7. In some cases, the UV/O₃ treated BCB showed slightly higher die shear strength (such as in case of CA-1). In other cases, the UV/O₃ treated surface did not show higher die shear strength. Overall, there was no significant difference in die shear strength between UV/ozone treated BCB and untreated BCB among all the underfills tested.

Polyimide passivated silicon dies without cleaning or UV/ozone treatment were also used for die shear test. The die (1.2 × 1.2 mm) was smaller than the BCB passivated silicon die. The test results are shown in Fig. 8. The interfacial failure between underfill and polyimide passivation accounted for the majority part of the fractured surface. No failure at interface between polyimide and silicon was observed. The addition of CA-3 led to some decrease of interfacial adhesion between underfill and polyimide passivation. Addition of CA-1 and CA-2 had no obvious effect on the adhesion performance. However, addition of CA-4, CA-5 and CA-6 increased the die

shear strength between underfill and polyimide passivation by 20%.

The die shear samples of underfill to polyimide passivation were placed in an 85 °C/85% relative humidity chamber for 500 h. The die shear tests were performed after aging. The results are also shown in Fig. 8. Without coupling agent or with the three silane coupling agents, the adhesion strength did not decrease after aging at 85 °C/85% RH for 500 h. However, with the addition of titanate or zirconate coupling agent, the adhesion strength dropped by 40–50% after aging. The addition of titanate or zirconate coupling agent was harmful to the interfacial adhesion during aging, although it improved the adhesion before aging in an 85 °C/85% relative humidity environment. This is related to the moisture absorption of the underfill and hydrolysis of the CA during aging in an 85 °C/85% relative humidity environment. With the addition of titanate or zirconate coupling agents, the moisture absorption during 85/85 aging increased dramatically. Also, the chemical bond formed between titanate or zirconate coupling agent with substrate (Ti–O–R or Zr–O–R) can be easily hydrolyzed, leading to decrease in adhesion strength after 85/85 aging.

IV. CONCLUSIONS

Coupling agents under investigation affected the curing and bulk property of the underfill. Amino functionalized zirconate coupling agent CA-6 catalyze the curing reaction of epoxy underfills. Addition of coupling agents led to a decrease in glass transition temperature of the underfill material, especially for CA-5 and CA-6. Addition of CA-4 deteriorated the thermal stability of the underfill material. Addition of coupling agents increased the moisture absorption of epoxy underfill material. Addition of titanate and zirconate coupling agents improved adhesion of epoxy underfill with BCB passivated silicon. However, with the addition of titanate and zirconate coupling agents, the adhesion strength of underfill with polyimide passivation decreased greatly after aging in an 85 °C/85% RH environment.

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